Practical solid oxide fuel cells with anodes derived from self-assembled mesoporous-NiO-YSZ

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Solid oxide fuel cells comprised of an anode made from sintered and reduced mesoporous-NiO-YSZ are shown to provide stable current and power densities at the operating temperature of 800 °C and show better performance than cells with anode cermets made from mechanical mixtures of NiO and YSZ, attributable to the unique anode microstructure.

Since the discovery of the MCM class of mesoporous silicas by Mobil Oil Corporation in 1992,[1] surfactants have been used to template a wide variety of periodic mesostructured and mesoporous materials.[2] Generally, with few notable exceptions, attempts to prepare mesoporous transition metal oxides by surfactant-based self-assembly methods yield materials that are not thermally stable and collapse upon surfactant removal.[3] Amphiphilic poly(alkylene oxide) block copolymers have also been employed as structure-directing agents in the preparation of more robust mesostructures having thicker and nanocrystalline channel walls.[4]

Recently, we were first to report the synthesis and characterization of mesoporous yttria-stabilized zirconia (YSZ) and M-YSZ materials, where M = Pt, NiO and Ni, which were synthesized by a co-assembly synthetic strategy using metal glycolate and metal salt precursors with a common cationic surfactant template under aqueous conditions.[5] These materials were found to exhibit unusual thermal stability, as high as 700–800 °C, for a mesoporous transition metal oxide prepared from a surfactant template. This was attributed to the co-crystallization and thickening of the YSZ channel walls as the surfactant and residual acetate/glycol ligands are lost to thermal oxidation in air. The mesoporous product, composed of nanocrystalline YSZ channel walls, has a typical BET surface area of about 260 m^2 g^{-1} for pure YSZ and surface areas ranging from 162–112 m^2 g^{-1} for materials containing 13–40 mol% Ni or NiO. Pressed powders of these materials were previously investigated for oxygen-ion and mixed conductivity by impedance spectroscopy.[6]

These high surface area mesoporous-M-YSZ materials, having a narrow pore size distribution, were envisioned to enhance fuel/oxidant mass transport to reactive sites and, through the amalgamation of YSZ, metal, and accessible pores, to enlarge the triple-phase boundary (TPB) region where charge transfer reactions occur. The TPB region is defined as the region bordering the oxygen ion-conductor, electron conductor, and gaseous reagents and is mainly responsible for polarization losses occurring at the electrodes.[7] As yet, there have been no reports for any SOFC electrodes comprised of a mesoporous YSZ-based material in any form. This is in part due to the high sintering temperature, usually 1400 °C, required for good adherence between the YSZ composite anode and the dense YSZ electrolyte as well as for the densification of YSZ in the anode.[8] Although SOFCs have been shown to reasonably operate at the low temperatures of 500 to 800 °C,[9] the incorporation of metastable materials, such as the aforementioned mesoporous-M-YSZ materials, without structural collapse is problematic and unattainable at the present.

Herein we report the sintered, reduced versions of surfactant-assembled mesoporous-NiO-YSZ materials[10] to be a unique

nanocomposite of metal and ceramic with a phase homogeneity much superior to metal–ceramic composites (cermets) made from mechanical mixing or other engineering techniques. The use of such composites as SOFC anodes may hold distinct advantages over traditional cermets due to their ease of synthesis and creation of a large TPB length at the interface of the nanodimensioned Ni and YSZ constituents.

Fig. 1 shows a high resolution-field emission-scanning transmission electron microscopy (HR-FE-STEM) image and the corresponding energy-dispersive X-ray spectroscopy (EDS) maps for a thin-sectioned mesoporous-NiO-YSZ sample, prepared by methods described elsewhere.[5] As evident from the EDS maps, nickel oxide is extremely well dispersed at the nanoscale within the mesoporous material, resulting in a compositionally single phased material.
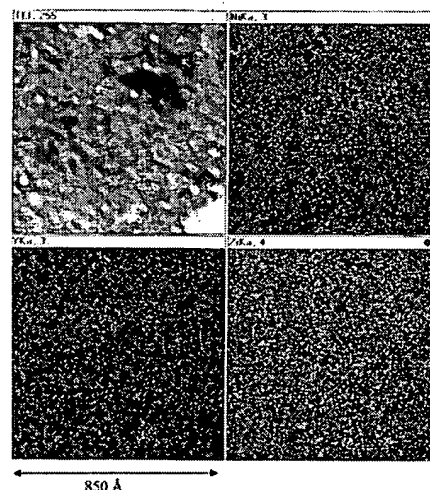

850 Å

Fig. 1 HR-FE-STEM image and corresponding EDS mapping for thin-sectioned mesoporous-NiO-YSZ.

Electrolyte-supported fuel cells used for this study were prepared using a dense 200 μm YSZ substrate (Ceraflex 8Y, Marketech Int., Inc). The anode, about 40–60 μm in thickness, was attached to the dense YSZ substrate at either 1150 or 1400 °C, as shown in the scanning transmission electron (SEM) micrographs in Fig. 2. The less sintered material has an average
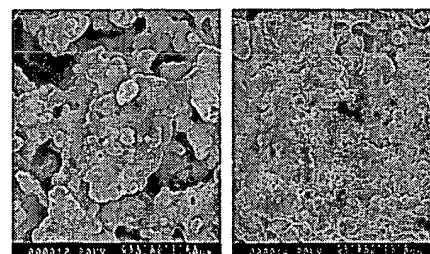

Fig. 2 SEM micrographs of mesoporous-NiO-YSZ-based anodes attached to a dense YSZ substrate at 1100 °C (left) and 1400 °C (right).

primary particle size of 100–150 nm and appears quite porous. Comparatively, the anode sintered at 1400 °C has micron size particles and its microstructure appears to be more highly sintered and dense, as had been expected. A composite cathode, of similar thickness to the anode, prepared from a 50:50 mixture of LSM ($La_{0.7}Sr_{0.3}MnO_3$, Marketech Int., Inc.) and YSZ (Tosoh Corp, TZ-8YS) was attached to the opposite side of the dense YSZ substrate by sintering to 1100 °C. Electrical contacts to both electrodes were made by Pt ink (Engelhard, #6082) and Pt mesh and wire. Each cell, having an active surface area of 1/3 cm², was sealed into an alumina tube of 1 cm inner diameter with zirconia-based adhesives (Aremco, Ceramabond 571 and Ultra-Temp 516). Humified hydrogen (3% H₂O) and air were used as the fuel and oxidant, respectively.

Current–voltage (I–V) characteristics are shown in Fig. 3, which compares the performance for cells at 800 °C made from a mesoporous-NiO-YSZ anode attached at either 1100 or 1400 °C. Both types of cells had reasonable open circuit voltages of about 1.07 V, however cells with the anode attached at 1100 °C resulted in much poorer performance as indicated by the non-linearities observed in the I–V curve.[11] The performance of this cell was observed to continually decrease over 4 h of operation at a constant voltage of 0.5 V. Cells with an anode attached at 1400 °C performed tremendously better as observed from the fairly linear I–V curve, especially at high current densities, giving a maximum current and power density of 717 mA/cm² and 153 mW/cm² at 800 °C or 300 mA cm⁻² and 60 mW cm⁻² at 700 °C. While maintaining a constant cell potential of 0.5 V, the performance of the cell was observed to be very stable over a 24 h period at the operating temperatures of 700 and 800 °C. These results suggest that the higher attachment temperature of the anode helps to prevent the sintering of the nickel component by providing better YSZ particle connectivity within the cermet, as also observed in Fig. 2, and also better adhesion to the dense YSZ substrate. Briefly, the latter cell performs much better in comparison to cells made with anodes of similar composition prepared from a mechanical mixture of NiO and YSZ powders, which result in a maximum current and power density of less than 200 mA/cm² and 50 mW/cm² at 800 °C, quite similar to typical values also reported by others.[12]
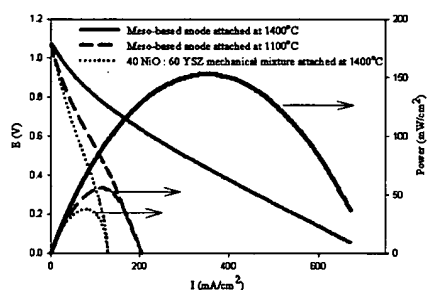

Fig. 3 I-V characteristics at 800 °C for cells made from mesoporous-NiO-YSZ-based anodes attached at 1100 and 1400 °C and mechanically mixed NiO/YSZ powders (40:60 vol. ratio) attached at 1400 °C.

The anodic activity at 800 °C was measured by impedance spectroscopy.[13] We observed a two semicircle response having a total electrode interfacial resistance (R_e) of 15.6 Ω cm², determined by taking the difference between the low and high frequency intercepts, and an ohmic resistance of 0.7 Ω cm², determined from the high frequency intercept.

Upon concluding the operation of the better performing cell, we analyzed the composite anode by TEM and electron spectroscopic imaging (ESI). The anode was removed from the dense YSZ substrate, embedded in epoxy and thin-sectioned with an ultra-microtome. Fig. 4 shows the TEM image and corresponding electron energy loss spectroscopy (EELS) maps for Y and Ni. Nickel metal still appears to be relatively well dispersed at the nanoscale within the thin-sectioned anode particles.
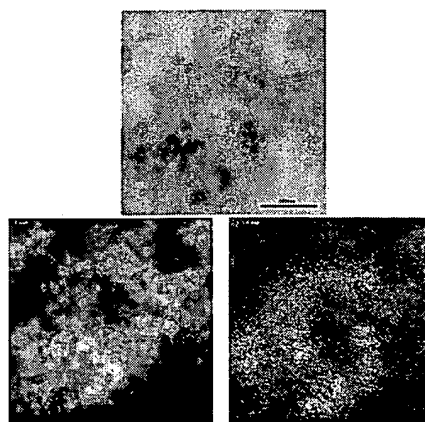

Fig. 4 TEM image (top) and corresponding EELS maps for the elements Y (left) and Ni (right).

These results illustrate, for the first time, that sintered and densified versions of co-assembled mesoporous-NiO-YSZ have improved microstructural features compared to traditional cermet anodes including nanoscale homogeneity of Ni and YSZ components. Cells with anodes based on these composites show better performance than cells with anode cermets made from mechanical mixtures of NiO and YSZ. Further optimisation of the to the anode/electrolyte interface could boost the cell performance further.

Notes and references

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13 Impedance spectroscopy measurements were performed using a Solartron frequency response analyzer (model 1260) and electrochemical interface (model 1286) over the frequency range 10⁷ to 10⁻¹ Hz using a perturbation voltage of 10 mV. For this purpose, a cell was prepared having a 3-electrode configuration with RF sputtered Pt counter (0.57 cm²) and reference (0.19 cm²) electrodes on the air side of the YSZ substrate and a working electrode (0.07 cm²) on the fuel side made of mesoporous-NiO-YSZ attached at 1400 °C.